(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 199651909 B2
(10) Patent No. 704063

(54) Title
Water-based ink composition for marking supports

(51)[6] International Patent Classification(s)
C09D 011/10

(21) Application No: 199651909

(22) Application Date: 1996 .04 .26

(30) Priority Data

(31) Number	(32) Date	(33) Country
95 04990	1995 .04 .26	FR

(43) Publication Date : 1996 .11 .07
(43) Publication Journal Date : 1996 .11 .07
(44) Accepted Journal Date : 1999 .04 .15

(71) Applicant(s)
Imaje S.A.

(72) Inventor(s)
Alain Heraud; Pierre de Saint Romain

(74) Agent/Attorney
F B RICE and CO,605 Darling Street,BALMAIN NSW 2041

(56) Related Art
US 5004763
US 4996252
GB 2225788

AU9651909

(12) PATENT ABSTRACT (11) Document No. AU-A-51909/96
(19) AUSTRALIAN PATENT OFFICE

(54) Title
WATER-BASED INK COMPOSITION FOR MARKING SUPPORTS

International Patent Classification(s)
(51)[5] C09D 011/10

(21) Application No. : 51909/96 (22) Application Date : 26.04.96

(30) Priority Data

(31) Number	(32) Date	(33) Country
95 04990	26.04.95	FR FRANCE

(43) Publication Date : 07.11.96

(71) Applicant(s)
IMAJE S.A.

(72) Inventor(s)
ALAIN HERAUD; PIERRE DE SAINT-ROMAIN

(74) Attorney or Agent
F B RICE & CO , 28A Montague Street, BALMAIN NSW 2041

(57)

The invention relates to an ink composition for marking objects incorporating at least a binder, a pigment and/or a dye and a solvent essentially consisting of water, characterized in that the binder comprises the combination of a polymer resin in dispersion and a water-soluble polymer resin, preferably obtained by neutralization to make it soluble for at least part of the carboxyl groups carried by a water-insoluble polymer.

The invention also relates to a process for marking objects by projecting or spraying ink onto said objects and a substrate provided with a marking obtained by drying the ink composition.

DESCRIPTIVE ABSTRACT

The invention relates to an ink composition for marking objects incorporating at least a binder, a pigment and/or a dye and a solvent essentially consisting of water, characterized in that the binder comprises the combination of a polymer resin in dispersion and a water-soluble polymer resin, preferably obtained by neutralization to make it soluble for at least part of the carboxyl groups carried by a water-insoluble polymer.

The invention also relates to a process for marking objects by projecting or spraying ink onto said objects and a substrate provided with a marking obtained by drying the ink composition.

AUSTRALIA

Patents Act 1990

IMAJE S.A.

ORIGINAL

COMPLETE SPECIFICATION
STANDARD PATENT

Invention Title:

Water-based ink composition for marking supports

The following statement is a full description of this invention including the best method of performing it known to us:-

//

DESCRIPTION

The invention relates to an ink composition for marking all porous or non-porous supports, such as papers, cardboards, glass, plastics, metals or any other porous or non-porous surface, which is particularly appropriate for the ink jet marking of most supports.

Ink jet printing is well known and permits the printing, marking or decoration of all types of objects, at a high speed and without any contact between said objects and the printing device, with random variable messages such as bar codes, sell-by dates, etc., as well as on non-planar supports.

The ink jet printing systems can be subdivided into two major groups, namely "drop on demand" or DOD and "continuous jet" or CJ. The ingredients forming the inks for these printing systems are organic products, dyes or pigments, resins, in more or less volatile solvents or in water, whereby other additives can be incorporated such as those necessary for giving the ink the conductivity required for electrostatic deflection in the continuous jet method.

Ink compositions which can be applied by drop on demand methods, namely on the one hand piezoelectric systems using the deformation of a piezoelectric ceramic under the effect of a voltage in order to suck and spray the ink, and on the other "bubble jet" systems, are mostly water-based. Thus, the utilization of water permits the use of the most widely employed, water-soluble dyes. Other reasons for using water as the solvent medium for such inks are its price, its absence of toxicity and its low volatility. The inherent weakness of all these water-based inks is the sensitivity to water of the marking obtained. Therefore efforts have been made to improve the water resistance of inks used in the drop on demand procedure by using specific dyes and special combinations.

Thus, FR-A-2 305 479 describes an ink for a water-based ink jet printer, in which the dye is dissolved in a water-immiscible solvent with the addition of a complexing agent incorporating a long chain fatty acid salt and a wetting agent (sodium aryl sulphonate) by means of which a single phase is obtained.

The dried ink is insensitive to water in the wet friction or rubbing test.

Due to the fact that the inks used in the systems of the drop on demand type must have a low evaporation speed to prevent clogging of nozzles, their application is limited to porous supports penetrated by the ink and which can dry by absorption, which is not the case with non porous surfaces. Thus, the markings on non porous supports would be too easy to erase even by slight rubbing with the finger.

Printing systems of the continuous jet type rarely use water-based inks, because this technology is more suitable for high speed marking operations for which a high evaporation speed is required. Therefore these inks are usually based on organic solvents, particularly alcohols and ketones. The inks used in continuous jet systems have a good behaviour on all non porous support types to be marked.

Conventionally, this type of ink contains:

- solvent or a mixture of solvents, the majority solvent being very volatile and not very viscous, such as alcohols, ketones and esters with a low molecular mass making it possible to adjust the viscosity to a value of 2 to 10 mPa.s., more viscous and less volatile, majority solvents such as glycol ethers can be added to improve the drying of the ink on the support and water can sometimes be added to these formulations, but only in small proportions and never as a main solvent and in a majority quantity,
- one or more binders also called resins, because they are usually solid and polymeric, which makes it possible to ensure the adhesion of the ink to the supports in question and in particular on non porous supports, the nature of these binders, specific to each support category, giving the ink its resistance properties to physical and/or chemical action,
- one or more dyes and/or pigments to give the ink its colour, or particular optical properties such as fluorescence,
- optionally a "conductivity" salt.

With regards to the inks whose main solvent is water, there are also water-based, jet sprayable inks.

It is desirable to formulate inks for printing by ink jet incorporating water as the majority solvent. Thus, the use of organic solvents causes toxicity and inflammability problems.

The use of organic solvents is harmful to the environment, because after the ink has been applied to the support, the solvent evaporates and releases its volatile constituents into the atmosphere. Volatile organic compounds are subject to ever more strict regulations tending towards the complete banning thereof, as is the case with chlorine solvents.

Thus, EP-A-466 341 describes an ink for ink jet printing having a low volatile solvent content comprising an aqueous emulsion or dispersion of a resin with a particle size of 0.01 to 1 µm. This resin is of the polyester, styrene-acrylic, aromatic or aliphatic polyurethane, alkide, epoxy, vinyl or phenolic type.

The dye is a soluble dye or a pigment dispersion, more particularly carbon black. The inks obtained give markings having a good resistance to water and solvents, even without subsequent hardening on non porous supports.

US-A-4 365 035 relates to an aqueous ink composition for ink jet printing comprising an aqueous dispersion of a white pigment having a particle size below 5 um (micrometers), as well as a binder in the form of acrylic resin.

The "RESEARCH DISCLOSURE", December 1980, p 540, abstract 20033, Havant, Hampshire, GB describes an aqueous ink for ink jet printing containing a carbon black dispersion, an acrylic resin in dispersion and polyethylene glycol for preventing ink deposits and clogging. EP-A-286 219 relates to a pigment-free, opaque ink composition for ink jet printing comprising hollow microspheres of a random polymer with an external diameter between 0.4 and 1 µm (micron) and which makes it possible to obtain markings adhering to porous and non porous supports without any of the clogging and sedimentation problems generally observed with dense pigments. The binder is in the form of a resin dispersion or emulsion, particularly of styrene-acrylic resin.

US-A-4 136 076 relates to an aqueous ink composition for jet printing having

an excellent resistance and which comprises as the binder solubilized acrylic polymers or copolymers crosslinked during drying by a metal ion such as zinc.

It can be gathered from what has been stated hereinbefore that it is known to formulate inks for ink jet printing combining in the aqueous phase:
- soluble dyes or pigments in dispersion form such as carbon black,
- resins in dispersion, i.e. in the form of spherical particles with a diameter of approxiamtely 0.1 µm (micron), also called "emulsion" polymers,
- little organic solvent.

It is also known that it is possible to formulate inks with resins in aqueous solution, as is done in organic solvent.

The use of pigment placed in dispersion, or even in microemulsion form, has also long been known.

There are two main binder categories, namely hydrosoluble polymers and polymers in dispersion.

Hydrosoluble polymers have the advantage of permitting a solubilization of the dried ink in different elements of the hydraulic circuit of printers, more particularly continuous jet printers. Thus, in such printers, the ink passes out of a very small orifice under pressure, being subdivided into droplets, which are electrically charged and deflected for printing, or alternatively are not charged and recovered in a channel by suction and then recycled to the ink circuit. On stopping the printer, inevitably ink unused for the printing operation is left behind in the recovery tubes and this ink dries during the non-operative periods. Aqueous inks containing a hydrosoluble polymer as the binder consequently, in the same way as solvent-based inks, permit an easy dissolving of the ink dried in the ink circuit of the printer, whilst not having the aforementioned disadvantages associated with the use of a volatile organic solvent. However, hydrosoluble polymers have the major disadvantage of remaining soluble or highly soluble to water after their drying, particularly on non porous supports.

Aqueous inks containing polymers in dispersion as binders have mechanical

properties greatly superior to those of soluble binders. After drying, they give the ink film a high resistance to moisture, unlike hydrosoluble binders. However, if the ink is applied by means of a deflected continuous jet printer, unlike in the case of inks containing hydrosoluble polymeric binders, it is no longer soluble once dried and during the starting up again of the printer, it can no longer be dissolved or only by using powerful organic solvents.

There is clearly a need for ink compositions that permit rapid marking, so as to take maximum advantage of the printing capacity of ink jet printers, of objects with a surface of a porous nature such as papers and cardboards, but also objects having a non porous surface, such as plastics, glass and metals. There is also a need for an ink composition that permits a marking having a high resistance to moisture, particularly on non porous surfaces, using a water-based ink having the lowest possible content of volatile organic compounds, so as to satisfy toxicity, inflammability and environmental protection requirements. There is also a need for an aqueous ink also having a good adhesion and a goods resistance to chemical action. Preferably, all these properties should be obtained without affecting the properties normally required of inks for ink jet printers and in particular for those using the continuous jet method, namely viscosity, resistivity, etc. In order to permit high speed marking, the ink preferably has the maximum possible drying speed. There is also a need for an aqueous ink, which can easily be dissolved after drying in the ink circuit of printers without having to use, as in the case of inks incorporating polymers in dispersion, aggressive solvents liable to bring about a deterioration of the different elements of the hydraulic circuit of printers.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Disclosure of the Invention

In a first aspect, the present invention is directed to an ink composition for marking objects incorporating at least:

- a binder
- a pigment and/or a dye,
- a solvent essentially comprising water,

characterized in that the binder comprises the combination

a) of at least one polymer resin in dispersion, and

b) at least one water-soluble polymer resin resulting from a water-insoluble polymer resin and made soluble in water by neutralization.

In another aspect, the present invention is directed to a process for marking objects by spraying an ink onto them, characterized in that the sprayed ink is an ink composition according to the first aspect of the invention.

The ink composition can optionally comprise an organic solvent having a coalescence agent function, i.e. permitting a good formation of the ink film by softening the polymer particles in dispersion.

Due to the fact that the ink uses as the binder polymers in dispersion, the inks have interesting mechanical properties and which are in all cases superior to those of inks including solely soluble binders, a good adhesion to all supports, even non porous supports, as well as remarkable wet rubbing resistance characteristics. Due to the combination of a non-soluble polymer in dispersion and a soluble polymer, the ink dried in the different elements of the printer can be more easily resolubilized without using aggressive solvents. The use in the inks according to the invention of pigments such as carbon black further improves their sensitivity to water after drying as compared with inks using water-soluble dyes, which greatly influence the water resistance of the deposited ink. The bar code readability of the markings obtained is remarkable and superior to all known inks. Finally, this ink is a water-based ink with all the resulting advantages of cost, toxicity and environmental acceptance.

The polymer in dispersion can be chosen from among acrylic and methacrylic polymers and acrylic and methacrylic copolymers with one another or with other ethylenically unsaturated monomers and in particular styrene, acrylates and methacrylates, vinyl polymers and copolymers, polyesters, aliphatic and aromatic polyurethanes, alkide and epoxy resins, etc. In order to co- adjust both the formation temperature of the film and its mechanical properties, it would be possible to use combinations of several types of resins in dispersion differing by their glass transition temperature (Tg) and their hardness. The glass transition temperature of these resins can vary within wide limits, e.g. between -50 and +100°C. Preferably, one of the resins or polymer in dispersion will have a glass transition temperature below 0°C or one of the polymers in dispersion will have a glass transition temperature above 50°C.

It is clear that the term dispersion also includes "microemulsion". Thus, the distinction between "dispersion" and "microemulsion" is frequently only a question of the particle size.

The dyes and/or pigments and their combinations can be chose so as to obtain the desired colour hue.

The dyes are e.g. those appearing in the "Colour Index Guide" under the category of "Pigment dyes" or "Disperse dyes". As the use of water-soluble dyes very considerably influences the water sensitivity of the deposited ink, even after drying, it is of interest to use pigment dispersions and in particular carbon black or phthalocyanine blue dispersions in order to obtain an insensitivity to water after drying. The dye and/or pigment quantity is preferably 0.1 to 15% and even more preferably 2 to 10 wt.%.

The soluble polymer is the second essential constituent of the inks according to the invention permitting the solubilization of the ink dried in the printer. Preferably, said polymer is prepared from a water-insoluble polymer resin (solubilization polymer) and rendered soluble in water by neutralization. In order not to lose its water resistance properties, said polymer will preferably also be insensitive to water after drying. Thus, preference is given to the use of a polymer solubilized by neutralization with a volatile product.

For example, the solubilizable polymer will be chosen from among acrylic and methacrylic polymers, as well as acrylic and methacrylic copolymers with one another or with other ethylenically unsaturated monomers and in particular styrene, methacrylates and acrylates, polyesters, aromatic or aliphatic polyurethanes, vinyl polymers and copolymers, silicones, chlorinated polyolefins, alkyl resins, epoxy resins, colophony and its derivatives.

In the most common case, these copolymers carry carboxyl functions, so that they e.g. have an acid number between 40 and 350. The polymers are made hydrosoluble by neutralizing at least part of the carboxyl functions with a base.

The preferred bases are ammonia and all primary, secondary and tertiary amines, particularly dimethyl ethanol amine, triethanol amine or 2-amino-2-methyl-1-propanol.

The weight ratio between the emulsion polymers and the solution polymers can vary within very wide limits and is in particular a function of the jet spraying equipment in which the ink is to be used and can be optimized for said equipment. This ratio determines both the resolubility of the ink after a given time, as well as the water resistance and mechanical properties. As the dispersions contain a known percentage of solid matter as indicated by the supplier, this weight ratio is expressed as dry matter to dry matter. It is possible to establish that the ratio of the solubilizable resin to the resin in dispersion is preferably between 0.25 and 4. With a ratio below 0.25, the resistance of the marking to water is excellent, but the resolubility is inadequate to permit a faultless operation in the printer. With a ratio exceeding 4, the resolubility is perfect and the operation in the printer is excellent, but the mechanical resistance of the marking (resistance to dry and wet rubbing, flexibility) is not as good.

The choice of all these ingredients and in particular resins forming the binder is in general terms dictated by their solubility in the medium and their compatibility with one another. The quantities to be used in the overall ink composition are mainly conditioned by the viscosity and optionally the conductivity to be obtained in order to be applied e.g. by jet printing.

The viscosity is preferably between 2 and 10 mPa.s over the complete operating temperature range for printers and the quantities of the ingredients could be easily determined by the expert so as to obtain an adequate viscosity. A preferred ink composition according to the invention would comprise, the percentages being weight percentages: 0.1 to 30% polymer resin in dispersion, 0.1 to 30% soluble resin, 0.1 to 15% dye and/or pigment, and the remainder to 100% solvent.

It is also obvious that resins other than those indicated hereinbefore can be incorporated into the ink composition according to the invention in order to

improve certain properties thereof.

When the ink is to be applied by continuous jet, it must have an adequate electrical conductivity, preferably 500 to 2000 µS/cm or higher.

The products giving the ink the necessary conductivity for spraying by continuous jet are ionizable compounds such as single or quaternary alkali metal, alkaline earth or ammonium salts, in the form of halides, perchlorates, nitrates, thiocyanates, acetates, sulphates, propionates, etc. Thus, if necessary, the products will be present in the ink composition so as to give it the aforementioned conductivity.

Another difficulty to be overcome in such compositions is the formation of foam. Thus, the composition according to the invention could optionally incorporate an antifoaming agent in a quantity of preferably 0.05 to 20 wt.%. There are numerous products having an antifoaming activity and in particular simple solvents such as isopropanol, 2-ethyl hexanol or 2-butanol, as well as silciones, oxyacetylene polyols, or organic solvents having a high boiling point such as butoxy-ethanol.

The aqueous medium favours the proliferation of microorganisms, so that it is preferable to add biocides, such as bactericides and fungicides to the aqueous inks according to the invention. These biocides, bactericides and fungicides will preferably be present in a quantity of 0.05 to 5 wt.%.

As mentioned hereinbefore, the ink can optionally comprise an organic solvent in a proportion preferably not exceeding 5 wt.%. This organic solvent essentially serves as a coalescence agent, i.e. it permits the satisfactory formation of the ink film by the softening of the polymer particles in dispersion. This solvent can be chosen from among glycol ethers and in particular ethylene or propylene glycol and their esters.

The invention also relates to a process for marking porous or non porous objects by spraying onto the same an ink composition of the type described hereinbefore. Marking can in particular take place by the continuous jet method.

The invention also relates to a porous or non porous substrate or support provided with a marking incorporating the ink composition described hereinbefore. This substrate can be of metal, e.g. aluminium, steel (drink cans), glass (glass bottles), wood, ceramic, paper, cardboard, synthetic polymer (plastics), such as PVC, PET, polyolefin such as polyethylene (PE), polypropylene (PP), Plexglas, or any other porous or non porous substance.

The invention will be better understood from reading the following description of non-limitative embodiments.

The following ink compositions containing different types of binder have been prepared by mixing the products given in the following table 1.

TABLE 1

EXAMPLE NO.	1	2	3	4	5
30% black carbon black dispersion	18	18	18	18	18
Acrylic dispersion, Tg 23°C, 45% dry extract	20	10	16		8
Acrylic dispersion, Tg 50°C, 50% dry extract					8
34% dry extract polyurethane dispersion				28	
Acrylic resin, acid number 250				8	8
Styrene-acrylic resin, acid number 250	5	10	8		
Ammonia (28% NH_3)	5	5	5	5	5
Demineralized water	51.7	56.7	52.7	44.7	52.7
Antifoaming agent	0.2	0.2	0.2	0.2	0.2
Biocide	0.1	0.1	0.1	0.1	0.1
Solubilizable/dispersion resin ratio	0.5	2	1	1	1
Viscosity (mPa.s)	5.3	4.3	4.9	.6.5	5.5
Conductivity (mS/cm)	>5	>5	>5	>5	>5

All the percentages are weight percentages, unless indicated to the contrary, the viscosity being in mPa.s and the conductivity in mS/cm.

The thus prepared inks were tested in deflected continuous jet printers and make it possible to obtain excellent quality impressions. The markings obtained with example 1 are the most water resistant and those of example 2 offer excellent results when used in a printer. Examples 3, 4 and 5 offer a good compromise between the water resistance and the machinability. Example 4 gives markings more suitable for flexible supports than those of example 5, which have a better high temperature resistance.

The following ink compositions containing different types of neutralization amines were prepared by mixing the products given in the following table 2.

TABLE 2

EXAMPLE NO.	6	7	8	9
Carbon black dispersion	18	18	18	18
Acrylic dispersion, tG 23°C, 45% dry extract	14	14	14	14
Styrene-acrylic resin, acid number 250	7	7	7	7
Demineralized water	55.7	55.7	55.7	55.7
Ammonia (28% NH_3)	5			
Dimethyl ethanol amine		5		
Triethanol amine			5	
2-amino-2-methyl-1-propanol				5
Antifoaming agent	0.2	0.2	0.2	0.2
Biocide	0.1	0.1	0.1	0.1
Viscosity (mPa.s)	4.0	4.3	4.6	5.1
Conductivity (mS/cm)	5	5	5	5

All the percentages are weight percentages, unless indicated to the contrary, the viscosity being in mPa.s and the conductivity in mS/cm.

The thus prepared inks were tested in deflected continuous jet printers and lead to impressions of excellent quality. All have the same resistance to water after drying. However, complete drying is more rapidly obtained with

ammonia than with the other bases, the slowest drying being with 2-amino-2-methyl-1-propanol.

Other ink compositions (examples 10 to 14) containing different types of pigments and antifoaming agents were prepared mixing the products given in the following table 3.

TABLE 3

EXAMPLE NO.	10	11	12	13	14
Carbon black dispersion		18	18	18	18
Phthalocyanine blue dispersion	15				
Acrylic dispersion Tg 50°C, 50% dry extract	16	16	16	16	14
Acrylic resin, acid number 250	8	8	8	8	7
Demineralized water	60.7	57.5	57.7	57.7	56
Acetylene diol antifoaming agent		0.4			
Silicone antifoaming agent	0.2		0.2		
2-ethyl hexanol				2	
2-butanol					5
Biocide	0.1	0.1	0.1	0.1	
Viscosity (mPa.s)	4.7	4.2	4.2	4.6	5.2
Conductivity (mS/cm)	5	5	5	5	4

All the percentages are weight percentages, unless indicated to the contrary, the viscosity being in mPa.s and the conductivity in mS/cm.

The thus prepared inks were tested in deflected continuous jet printers and lead to excellent impressions without any variation of the wetting capacity of these inks on supports such as polyethylene, PET or PVC.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Ink composition for marking objects incorporating at least:
- a binder,
- a pigment and/or a dye,
- a solvent essentially comprising water,
characterized in that the binder comprises the combination a) of at least one polymer resin in dispersion and b) at least one water-soluble polymer resin resulting from a water-insoluble polymer resin and made soluble in water by neutralization.

2. Ink composition according to claim 1, characterized in that it also comprises a conductivity salt.

3. Ink composition according to claim 1, characterized in that it comprises an additive chosen from among an antifoaming agent, a biocide, bactericide or fungicide, a chemical stabilizer, a UV stabilizer, considered singly or in combination.

4. Ink composition according to claim 1, characterized in that the dye and/or pigment is in the form of a dispersion of one or more pigments in water.

5. Ink composition according to claim 1, characterized in that it also comprises an organic solvent.

6. Ink composition according to claim 1, characterized in that the polymer in dispersion has a glass transition temperature Tg between -50 and +100°C.

7. Ink composition according to claim 1, characterized in that the resin in dispersion is chosen from among styrene, acrylic and methacrylic polymers and copolymers with one another or with other ethylenically unsaturated monomers, vinyl polymers and copolymers, polyesters, aromatic and aliphatic polyurethanes, alkide resins and epoxy resins.

8. Ink composition according to claim 1, characterized in that the water-

soluble polymer resin results from a water-insoluble polymer resin carrying carboxyl functions (solubilizable resin) and made soluble in water by the neutralization of at least part of its carboxyl groups.

9. Ink composition according to claim 1, characterized in that the resin made soluble by neutralization is chosen from among styrene, acrylic and methacrylic polymers and copolymers with one another or with other ethylenically unsaturated monomers, polyesters, vinyl polymers and copolymers, aromatic and aliphatic polyurethanes, alkide resins, epoxy resins, chlorinated polyolefins, silicones, colophony and its derivatives.

10. Ink composition according to claim 8, characterized in that the solubilizable resin has an acid number between 40 and 350.

11. Ink composition according to claim 8, characterized in that the solubilizable resin is made soluble in water by neutralization with a base chosen from among ammonia, primary, secondary and tertiary amines.

12. Ink composition according to claim 2, characterized in that the conductivity salt is chosen from among halides, perchlorates, nitrates, thiocyanates, acetates, propionates, and sulphates of single or quaternary ammonium, alkaline earth or alkali metals, considered single or in combination.

13. Ink composition according to claim 3, characterized in that the antifoaming agent is chosen from among silicones, oxyacetylene polyols and high boiling point organic solvents considered singly or in combination.

14. Ink composition according to claim 3, characterized in that the biocide, bactericide or fungicide are present in a quantity of 0.05 to 5 wt.%.

15. Ink composition according to claim 4, characterized in that the pigment in dispersion is a carbon black.

16. Composition according to claim 4, characterized in that the pigment in dispersion is a phthalocyanine blue.

17. Ink composition according to claim 5, characterized in that the organic solvent is chosen from among glycol ethers and their esters.

18. Ink composition according to claim 6, characterized in that one of the polymers in dispersion has a glass transition temperature (Tg) below 0°C.

19. Ink composition according to claim 6, characterized in that one of the polymers in dispersion has a glass transition temperature (Tg) above 50°C.

20. Ink composition according to claim 1, characterized in that the weight ratio of the soluble resin to the resin in dispersion is between 0.25 and 4.

21. Ink composition according to claim 5, characterized in that the organic solvent is present in a quantity not exceeding 5 wt.%.

22. Ink composition according to claim 1, characterized in that it comprises, the percentages being weight percentages relative to the total weight of the composition, 0.1 to 30% polymer resin in dispersion, 0.1 to 30% soluble resin, 0.1 to 15% dye and/or pigment and the residue to 100% solvent.

23. Ink composition according to claim 22, characterized in that the pigment and/or dye quantity is 2 to 10 wt.%.

24. Process for marking objects by spraying an ink onto them, characterized in that the sprayed ink is an ink composition according to any one of the claims 1 to 23.

25. Process according to claim 24, characterized in that marking takes place by the continuous jet method.

26. Substrate, characterized in that it is provided with a marking obtained by drying the ink composition according to any one of the claims 1 to 23.

27. Substrate according to claim 26, characterized in that the substrate is paper, cardboard, plastic, ceramic, wood, metal, or any other porous or non porous material.

DATED THIS 26 day of April 1996

IMAJE S.A.
Patent Attorneys for the Applicant:-
F B RICE & CO